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Japanese (PDF)

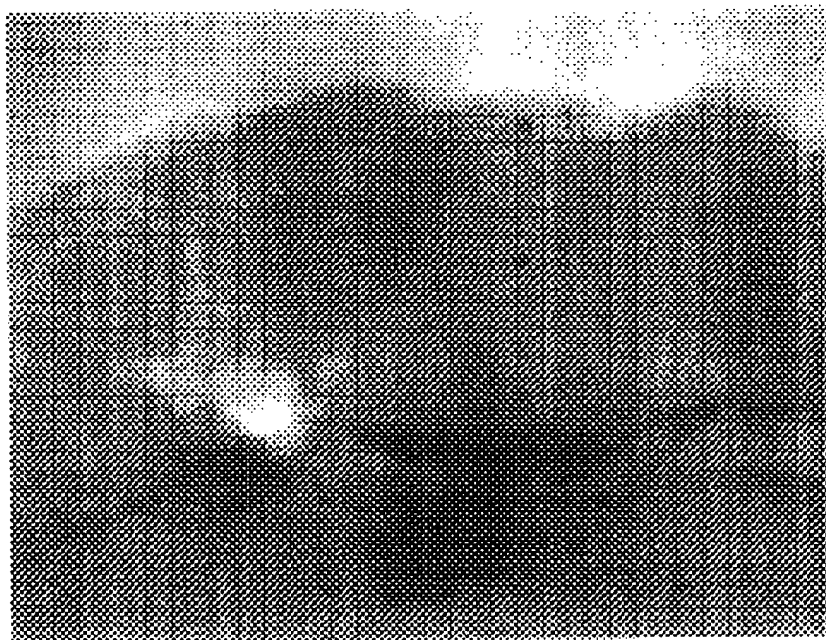
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FULL CONTENTS CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART
EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

Drawing selection drawing 1 ▾

図1 酸化皮膜断面図



[Translation done.]

Report Mistranslation

Japanese (whole document in PDF)

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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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CLAIMS

[Claim(s)]

[Claim 1] The with a specific inductive capacity of 20 or more high dielectric constant compound aluminum oxide coat which contains the central atom of ANION of inorganic oxo acid salt one to 50weight %.

[Claim 2] The high dielectric constant compound aluminum oxide coat according to claim 1 with which ANION of inorganic oxo acid salt is chosen from nitric acid, phosphorus acid, boric acid, vanadium acid, or tungstic acid.

[Claim 3] The manufacture method of the high dielectric constant compound aluminum oxide coat characterized by carrying out electrolysis anodization of the aluminum in the nonaqueous electrolyte of 5 or less weight % of the amounts of moisture containing inorganic oxo acid salt.

[Claim 4] The manufacture method of a high dielectric constant compound aluminum oxide coat according to claim 3 that inorganic oxo acid salt is chosen from a nitrate, an orthophosphate, borate salt, vanadium acid salt, or tungsten acid chloride salt.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to a high dielectric constant compound aluminum oxide coat and its manufacture method. A high dielectric constant compound aluminum oxide coat is used as the electrolytic condenser with which high electric capacity is demanded, the printing capacitor on a printed circuit board, the dielectric resonator for microwave, IC, the dielectric of a liquid crystal TFT, and an insulator.

[0002]

[Description of the Prior Art] Anodization of aluminum is the principle known well for many years, and is used in many fields industrially. Anodization is usually carried out in the

electrolysis solution of a basin system, and it is known that two kinds of oxidization coats called a porous type and barrier type by the kind of electrolysis solution to be used will be formed. Since a barrier type coat is precise and electric insulation is high, it is applied to the dielectric film of an electrolytic condenser, the insulating film of the aluminum wiring on a semiconductor, etc.

[0003] An aluminium electrolytic capacitor the aluminum foil which carried out surface roughening of the surface electrochemically or chemically A way acid system, the transformation which carried out anodization processing in the solution of the phosphorus acid system or an adipic acid system, and formed the aluminum oxide coat layer -- foil is used for the anode side electrode (surface-of-metal technical manual 671-page (1976) Nikkan Kogyo Shimbun, experiment surface technology 35 (6), 261 (1988)).

[0004] Generally the electric capacity C of a parallel board capacitor is defined by $C = \epsilon_0$ and $\epsilon_r A/d$ (however, the dielectric constant of an ϵ_0 ; vacuum, ϵ_r ; specific inductive capacity, A ; electrode surface product, d ; thickness of a dielectric). In order to obtain the capacitor of high electric capacity, it becomes the method whether the specific inductive capacity of (1) dielectric is raised, (2) surface areas are expanded, or to make it thin. The specific inductive capacity of an aluminum oxide is 7-10, and since electric strength will fall if an oxidization coat is made thin, high electric capacity-ization has been attained by expanding an electrode surface product by electrolysis etching.

[0005]

[Problem to be solved by the invention] However, in the flow of small-and-light-izing of an electric device in recent years, the demand of chip-izing and a miniaturization of an electrolytic condenser is strong, and, for that purpose, the further high electric capacity-ization of electrode foil is desired. Moreover, the same technical problem also as the dielectric film and insulating film on a printed circuit board circuit or a semiconductor circuit occurs. This invention will offer the high dielectric constant compound aluminum oxide coat which can respond to such a request, and its process.

[0006]

[Means for solving problem] That is, the 1st of this invention offers a with a specific inductive capacity [containing the central atom of ANION of inorganic oxo acid salt] of 20 or more high dielectric constant compound aluminum oxide coat. The 2nd of this invention offers the method of manufacturing a high dielectric constant compound aluminum oxide coat, by carrying out electrolysis anodization of the aluminum in the nonaqueous electrolyte of 5% or less of the amount of moisture containing inorganic oxo acid salt.

[0007]

[Function] In anodization by the system or the very small quantity system in which water does not exist, the oxygen which forms ANION of the inorganic oxo acid salt which is **** of an

electrolysis solution can serve as a source of oxygen. Therefore, the central atom of ANION of this oxo acid salt contains with the oxygen atom which forms ANION of inorganic oxo acid salt by anodization, and specific inductive capacity increases sharply [specific inductive capacity] or more to 20 highly more than 2 double compared with the conventional aluminum oxide.

[0008] (Outline of invention)

The high dielectric constant compound aluminum oxide coat of manufacture method this invention of a high dielectric constant compound aluminum oxide coat is obtained by carrying out electrolysis anodization of the aluminum in the nonaqueous electrolyte of 5% or less of the amount of moisture containing inorganic oxo acid salt.

[0009] As a nonaqueous electrolyte used for the method of this invention, the nonaqueous system solvent solution of inorganic oxo acid salt is used. As the above-mentioned inorganic oxo acid salt, 1 of inorganic oxo acid, 2, 3 or the ammonium salt of the 4th class, alkaline metal salt, the fourth class phosphonium salt, and sulfonium salt can be illustrated. As inorganic oxo acid which forms ANION of inorganic oxo acid salt Central atoms may be nonmetallic oxo acid, such as nitrogen, a phosphorus, and boron, like nitric acid, phosphorus acid, and boric acid, or a central atom may be oxy acid of metal, such as chromium, vanadium, and tungsten, like chromic acid, vanadium acid, and tungstic acid. Moreover, oxo acid may be Pori acid and iso Pori acid or heteropoly acid is further sufficient as it.

[0010] As a nonaqueous system solvent, alcoholic solvent; gamma-butyrolactone, such as ethylene glycol and methyl cellosolve, Lactone system solvents, such as gamma-BARERO lactone and delta-BARERO lactone; Ethylene carbonate, Carbonate system solvent; N-MECHIRUHORUMU amide, such as propylene carbonate and butylene carbonate, N-ethyl HORUMU amide, N, and N-JIMECHIRUHORUMU amide, N, and N-JIECHIRUHORUMU amide, Amide system solvent; 3-METOKISHIPUROPIONI trills, such as N-MECHIRU aceto amide, N, and N-JIMECHIRU aceto amide and N-MECHIRU pyrrolidinone, Nitril system solvents, such as a guru TARONI trill; phosphoric-ester system solvent; Trimethyl phosphate, triethyl phosphate, etc. reach. Although non-polarity solvents, such as polar solvents, such as a mixture of two or more sorts of these solvents, and HEKISAN, toluene, and silicon oil, can be illustrated, the polar solvent which is easy to dissolve inorganic oxo acid salt is more desirable.

[0011] Although the concentration of the inorganic oxo acid salt to be used changes with the degree of **** of the electrolysis solution which should be obtained, and sparking voltage, generally below concentration of saturated solution preferably 0.1-2mol/ it comes out. Moreover, in order to obtain a high dielectric constant compound aluminum oxide coat, the electrolysis solution needs to be anhydrous substantially and it is necessary to carry out the amount of moisture of an electrolysis solution to 2 or less weight % preferably 5 or less weight %. Specific inductive capacity of a high dielectric constant compound aluminum oxide coat can

be made still higher by reducing the amount of moisture. If there are too many amounts of moisture, in order to form the conventional oxidization coat which makes moisture the source of oxygen, the specific inductive capacity of the oxidization coat obtained does not improve. Generally, the temperature range of anodization is room temperature -150 degree C in above ***** , and it is current density 0.5 - 50 mA/cm². It is carried out in the range. Electrolysis anodization time is set by the electrode surface product.

[0012] By the method of the high dielectric constant compound aluminum oxide coat above, 20 or more specific inductive capacity which contains the central atom of ANION of inorganic oxo acid salt one to 50weight % can obtain 30 or more high dielectric constant compound aluminum oxide coats preferably. the film thickness of the high dielectric constant compound aluminum oxide coat of this invention -- transformation -- it is arbitrarily set with voltage and a 10-1000nm thing is obtained.

[0013] [the high dielectric constant compound aluminum oxide coat obtained by the above-mentioned method] The central atom of ANION of the inorganic oxo acid salt which is the electrolyte used in anodization, namely, -- a nitrate, an orthophosphate, or oxo acid salt like borate salt -- respectively -- nitrogen, a phosphorus, and boron -- moreover, with oxy acid salt like vanadium acid salt or tungstic acid salt, vanadium and tungsten are contained, respectively.

[0014]

[Working example] An example and a comparative example are given to below, and this invention is explained to it still in detail.

(Example 1) The ethylene glycol solution containing the tetraethyl ammonium salt of nitric acid of 1 molar concentration was prepared, decompression heating was carried out, and it dried. Moisture of the electrolysis solution at this time was 15 ppm. using this electrolysis solution -- aluminum foil -- 5 mA/cm² anodizing to 50V by constant current -- transformation -- foil was obtained.

[0015] the obtained transformation -- as a result of observation of the section by TEM (scanning transmission electron microscope) of foil, the coat was almost smooth, and surface area hardly changed anodization before, but film thickness was 20nm. this transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and the electric capacity at 120Hz was measured in LCR meter. The electric capacity at 120Hz is 4.1 micro F/cm². It was. Electric capacity and the specific inductive capacity for which it asked from film thickness are shown in Table 1.

[0016] (Example 2) The ethylene glycol solution containing the tetraethyl ammonium salt of the way acid of 1 molar concentration was prepared, decompression heating was carried out, and it dried. Moisture of the electrolysis solution at this time was 500 ppm. using this electrolysis solution and anodizing aluminum foil to 38V by the constant current of 5 mA/cm² --

transformation -- foil was obtained. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and the electric capacity at 120Hz was measured in LCR meter. The specific inductive capacity for which it asked like the example 1 is shown in Table 1.

[0017] (Example 3) The ethylene glycol solution containing the tetraethyl ammonium salt of the phosphorus acid of 1 molar concentration was prepared, decompression heating was carried out, and it dried. Moisture of the electrolysis solution at this time was 400 ppm. using this electrolysis solution and anodizing aluminum foil to 25V by the constant current of 5 mA/cm² -- transformation -- foil was obtained. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and the electric capacity at 120Hz was measured in LCR meter. The specific inductive capacity for which it asked like the example 1 is shown in Table 1.

[0018] (Example 4) The ethylene glycol solution containing the tetraethyl ammonium salt of the vanadium acid of 1 molar concentration was prepared, decompression heating was carried out, and it dried. Moisture of the electrolysis solution at this time was 0.9 weight %. using this electrolysis solution and anodizing aluminum foil to 60V by the constant current of 5 mA/cm² -- transformation -- foil was obtained. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and the electric capacity at 120Hz was measured in LCR meter. The specific inductive capacity for which it asked like the example 1 is shown in Table 1. FSTEM(**** radiation type scanning transmission electron microscope)-EDX (energy dispersion type X line segment light method) investigated the structure of the oxidization coat.

[0019] Drawing 1 is the sectional view of the oxidization coat by FSTEM. As a result of conducting ultimate analysis of the portion shown in 1-4 of drawing 1 by EDX, it is made an atomic ratio, respectively. 1 (O; 75.30%, aluminum; [22.15% of] V; 2.55%), 2 (O; 73.69%, aluminum; [25.08% of] V; 1.23%), It is 3 (O; 69.44%, aluminum; [29.38% of] V; 1.18%), and 4 (O; 3.56%, aluminum; [96.28% of] V; 0.16%), and vanadium which is the central atom of vanadium acid contained in the oxidization coat.

[0020] (Example 5) The ethylene glycol solution containing the tetraethyl ammonium salt of the tungstic acid of 1 molar concentration was prepared, decompression heating was carried out, and it dried. It was 1 weight % of moisture of the electrolysis solution at this time. using this electrolysis solution and anodizing aluminum foil to 38V by the constant current of 5 mA/cm² -- transformation -- foil was obtained. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and the electric capacity at 120Hz was measured in LCR meter. The specific inductive capacity for which it asked like the example 1 is shown in Table 1.

[0021] (Comparative example 1) transformation -- as the ** electrolysis solution -- the object for aluminium electrolytic capacitors -- transformation -- using 10weight % of the adipic acid

ammonium solution currently used for manufacture of foil -- transformation -- voltage was set to 75V, and also aluminum foil was anodized like the example 1. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and electric capacity was measured in LCR meter. The electric capacity at 120Hz is 0.088 micro F/cm². It was. Moreover, the film thickness of observation of the section by TEM to the coat was 80nm, and electric capacity and the specific inductive capacity for which it asked from film thickness were 8.0.

[0022] (Comparative example 2) transformation -- the vanadium acid tetraethyl ammonium solution of 1 molar concentration was used as a ** electrolysis solution, and also aluminum foil was anodized to 50V like the example 1. the obtained transformation -- foil was dipped in 10weight % of adipic acid ammonium solution, and electric capacity was measured in LCR meter. The electric capacity at 120Hz is 0.12 micro F/cm². It was, when asked for specific inductive capacity like the example 1, it was set to 7.4, and it was almost the same as the specific inductive capacity of a comparative example 1.

[0023]

[Table 1]

	化成液	比誘電率
実施例 1	硝酸テトラエチルアンモニウム / E G	9.0
実施例 2	ホウ酸テトラエチルアンモニウム / E G	8.0
実施例 3	リン酸テトラエチルアンモニウム / E G	7.0
実施例 4	バナジン酸テトラエチルアンモニウム / E G	6.0
実施例 5	タングステン酸テトラエチルアンモニウム / E G	3.0
比較例 1	アジピン酸アンモニウム水溶液	8.0
比較例 2	バナジン酸テトラエチルアンモニウム水溶液	7.4

E G ; エチレングリコール

[0024]

[Effect of the Invention] [the high dielectric constant compound aluminum oxide coat of this invention] the conventional basin system -- transformation -- by being the high coat of 20 or more specific inductive capacity more than 2 double, and using the high dielectric constant compound aluminum oxide coat of this invention rather than the oxidization coat formed with the ** electrolysis solution It becomes possible to realize the electrolytic condenser of small size with high electric capacity or the same high electric capacity in the same size.

[Translation done.]